

Contributions of Al and Ni segregation to the interfacial cohesion of Cu-rich precipitates in ferritic steels

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Abstract

We characterise the influence of the segregation behaviours of two typical alloying elements, aluminium and nickel, on the interfacial cohesive properties of copper-rich precipitates in ferritic steels, with a view towards understanding steel embrittlement. The first-principles method is used to compute the energetic and bonding properties of aluminium and nickel at the interfaces of the precipitates and corresponding fracture surfaces. Our results show the segregation of aluminium and nickel at interfaces of precipitates are both energetically favourable. We find that the interfacial cohesion of copper precipitates is enhanced by aluminium segregation but reduced by nickel segregation. Opposite roles can be attributed to the different symmetrical features of the valence states for aluminium and nickel. The nickel-induced interfacial embrittlement of copper-rich precipitates increase the ductile-brittle transition temperature (DBTT) of ferritic steels and provides an explanation of many experimental phenomena, such as the fact that the shifts of DBTT of reactor pressure vessel steels depend the copper and nickel content.

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I. INTRODUCTION

It has long been known that the copper content in steels leads to precipitation hardening. Copper is an element commonly occurring in steels either as an intentionally added alloying species or as an impurity. Nanoscale copper-rich precipitates are utilised to provide substantial precipitation hardening for high-strength low-alloy steels, which possess excellent impact toughness, corrosion resistance, and welding properties [1–3]. In contrast, copper-rich precipitates induce hardening and embrittlement effects in reactor pressure vessel steels (RPV) after neutron irradiation [4–6], thereby limiting the operational life of nuclear power plants. Therefore, understanding the properties of copper-rich precipitates is desirable.

Many investigations have provided insight into the hardening mechanism that results from copper-rich precipitation in ferritic steels. Molecular dynamics simulation has suggested that the major source of precipitation hardening is the dislocation core-precipitate interaction [7–9]. Dislocation core-precipitate interactions tend to induce the loss of screw dislocation slip systems and the transformation of the copper phase for larger body center cubic (BCC) copper-rich precipitates ($d > 3.3$ nm) while inducing polarised-to-nonpolarised transitions of screw dislocation core structures in precipitates for very small BCC copper-rich precipitates ($1.5 \text{ nm} < d < 3.3 \text{ nm}$) [10, 11]. In addition to the diameter of precipitates, the temperature and dislocation line characteristics are important to the dislocation core-precipitate interaction [12]. Experimental evidence relating to the dislocation core-precipitate interaction has been observed using transmission electron microscope (TEM) experiments. In situ TEM demonstrates dislocations pinned and curved with obtuse bow-out angles by BCC copper-rich precipitates with $d \sim 2$ nm [13, 14]. TEM observations also demonstrate that the transformation of copper phase and the appearance of dislocation loops are induced by precipitates with $d \sim 4$ nm [15]. The bow-out angle of the dislocation can further be used to estimate macroscopic hardening [15].

Many experiments have specifically studied the copper-rich precipitation embrittlement effect on RPV steels and model alloys. Positron annihilation experiments suggest strongly that copper-rich precipitates are responsible for irradiation-induced embrittlement [16]. The influence of nickel content on the embrittlement of RPV steels has also been found to be important [17–22], and the nickel and copper content in steels have a synergistic effect on the embrittlement tendency [23–26]. It has been reported that RPV steels with high nickel

content have a higher ductile-brittle transition temperature (DBTT) shift than low-nickel steels with same copper content irradiated using same neutron fluence [23]. However, the shifts in the DBTT are small for irradiated low-copper, high-nickel RPV steels that do not contain copper-rich precipitates [24]. Furthermore, a parametric study of model alloys after neutron irradiation (at a neutron fluence of $72 \times 10^{18} m^{-2}$) showed that DBTT shifts increase with nickel content and that the shift is visible from a threshold copper content of approximately 0.08 at.% [25, 26]. These results demonstrate clear evidence for a relation between embrittlement and copper and nickel contents. The influences of nickel on copper-rich precipitates have therefore attracted significant attention.

Microstructure experiments show that nickel can occur in the copper precipitates. Atom probe experiments on thermally aged model alloys demonstrate that the nickel is located in the core region of the BCC copper-rich precipitates during the initial growth stage and is rejected from the core to the interfacial region during growth and coarsening [27]. Observations on neutron-irradiated RPV steels demonstrate a higher nickel concentration in the copper precipitates than in thermally aged model alloys [27, 28]. Recently, a series of atom probe experiments have revealed the growing and coarsening behaviour of copper-rich precipitates in concentrated multicomponent alloys with high strength [29–35]. The nickel and other alloying elements have been observed to segregate at the interface of the precipitates. Moreover, phase-field [36] and Langer-Schwartz [37] simulations of copper precipitates nucleation also indicated nickel segregation at the interface of copper precipitates during growth. First-principles calculation is very efficient in predicting the embrittlement potential and aids in understanding the mechanism of the impurity effect based on electronic structure [38–43]. These findings motivated us to perform a careful, first-principles investigation of the contribution of segregation, especially of nickel, on the interfacial cohesive property of precipitates to better understand the effects of these precipitates on embrittlement.

In this paper, we study aluminium and nickel as typical alloying elements to examine the effect of segregation at the interface of copper-rich precipitates towards steel embrittlement. After calculating the segregation energies, we characterise the effect of aluminium and nickel on the interfacial cohesion of copper-rich precipitates and attempt to explain their bonding properties in terms of their electronic structures. Finally, we discuss the roles of aluminium and nickel in the embrittlement of ferritic steels. Our results suggest that the nickel-induced interfacial embrittlement process increases the DBTT of ferritic steels.

II. METHODS AND MODELS

Our first-principles calculations are based on density functional theory (DFT) [44, 45] and performed using the Vienna Ab-initio Simulation Package (VASP) [46] with a plane wave basis set [47, 48]. The electron exchange and correlation is described within the generalised gradient approximation (GGA) [49, 50], and the interaction between ions and electrons is described using the projector augmented wave method (PAW) [51]. The PAW potentials we chose are treated by considering Fe3d4s, Cu3d4s, Al3s3p and Ni3d4s as valence states. All calculations include spin polarisation. The structural relaxations of the ions are calculated by conjugate-gradient (CG) algorithm.

We model the coherent (001) interfaces between copper-rich precipitates and the ferritic matrix by designing $(2 \times 2 \times 10)$ multi-layered supercells composed of BCC copper and BCC iron (Fig. 1). The lattice constants of the supercells are set using the theoretical value for BCC iron. Our BCC iron value, 2.83 Å, is reasonably consistent with the experimental value, 2.86 Å [52]. These multilayer structures have a distance of 10 atomic layers between each interface, and this is determined by considering the balance of avoidance of the interface interaction and computational expense. The three structures illustrated in Figs. 1a-c correspond to the interfaces of precipitates with copper concentrations of 100, 75, and 50 at.%, respectively. The k-points sample for these supercells are Monkhorst-Pack grids $(6 \times 6 \times 1)$.

We create initial configurations of supercells modelling the alloying element ($M = \text{Al}, \text{Ni}$) in different sites by substituting M for the iron or copper atoms from $(2 \times 2 \times 10)$ supercells. We substitute M for the iron atom at site 1, to simulate the system of M in the bulk of the ferritic matrix. The distance from site 1 to the interface is five atomic layers, sufficient to avoid the interaction between M and the interface. Sites 2 and 3 are used to simulate M segregation at the interface toward the matrix and toward the precipitated phase, respectively. Site 4 is used to simulate M in the precipitated phase.

The formation energy is one of quantities typically used to describe the segregation behaviour. The formation energy (E^M) of M in the crystal is defined as:

$$E^M = E_{M+CR} - E_{CR} - (E_M - E_A) \quad (1)$$

where E_{M+CR} and E_{CR} are the total energies of the supercell with a substitution defect

M and defect-free supercell, while E_M and E_A are the energies per atom of equilibrium pure-element reference states. The formation energy is dependent on the reference states, which induce arbitrariness in the result [53]. It is usually difficult to choose the correct form of reference states when one calculates the formation energy to predict the segregation behaviour.

Here, a more efficient quantity, the segregation energy, is used to predict the segregation behaviour. The segregation energy (E_X^M) of M at site X can be written as:

$$\Delta E_X^M = E_{M-X}^{tot} - E_{M-matrix}^{tot} \quad (2)$$

where E_{M-X}^{tot} and $E_{M-matrix}^{tot}$ are the total energies of the supercells for M at site X in precipitated phase and that for M in the matrix, respectively. A negative segregation energy indicates that M can transfer from the matrix to site X, whereas a positive segregation energy indicates that M prefers to dissolve within the matrix. The segregation energy reflects the competitive capacity of trapping M between the matrix and the precipitated phase. This strategy has previously been used to predict partition behaviours between cementite and ferrite [53], and the method has been verified to be appropriate.

The embrittlement property of the interface can be obtained from the Griffith work separating the interface. Based on the Rice-Wang mode [54], the Griffith work is a linear function of the difference in segregation energy for the alloying element M at the interface (ΔE_I^M) and that at the fracture free surface (ΔE_F^M), $\Delta E_I^M - \Delta E_F^M$. An alloying element M with positive $\Delta E_I^M - \Delta E_F^M$ will reduce the cohesion of the interface and induce an embrittlement potency, or vice versa. For the embrittlement property, the segregation energies (ΔE_F^M) at the fracture free surface are needed. We construct an isolated fracture free (001) ferritic matrix by subtracting the copper-rich phase from ($2 \times 2 \times 10$) supercells representing the interface to calculate ΔE_F^M (Fig. 2).

In addition to energetic properties, we also analyse electronic structures to provide insights into the bonding properties. We focus on the charge density differences within the region of the interface and the fracture free surface as shown in Fig. 2. The charge density differences (Fig. 3) are obtained by subtracting the superimposed charge density from the self-consistent charge density of the relaxed structure. Fig. 3 shows the charge accumulation and depletion, which indicate the interatomic interactions.

III. RESULTS AND DISCUSSIONS

A. Segregation energy

Because the composition of copper-rich precipitates in ferritic steels has a wide range, we present the segregation behaviour properties at the interfaces of copper-rich precipitates with different compositions. We have computed the interfaces of BCC precipitates with 100, 75, and 50 at.% copper. The segregation energies of aluminium and nickel at the interfaces of precipitated phases with different compositions are listed in Tables 1 and 2. Apart from the total segregation energy (ΔE_X^M), we also present the chemical and mechanical contributions to the segregation energy. The chemical contribution to segregation is represented as $\Delta E_X^{chem,M}$, which is calculated based on the unrelaxed structure. The mechanical contribution to segregation is represented as $\Delta E_X^{mech,M}$, i.e., the difference in segregation energy between the unrelaxed and relaxed structures. The relaxation energies of the supercell, ΔE_{sc} , are also used when estimating the lattice distortion.

1. Aluminium segregation

The segregation energies (see ΔE_X^{Al} in Table 1) of aluminium at the interfaces of the precipitated phases are predicted to be negative, indicating that the presence of aluminium atoms at the interfaces is energetically favourable compared to that in the ferritic matrix. Moreover, the segregation energies of aluminium at the interfaces are lower than those in the core regions of the precipitates, indicating that the presence of aluminium atoms at the interface is more favourable than that in the core region. These results indicate that the interface between the matrix and the precipitated phase can trap aluminium atoms, consistent with three-dimensional atom probe (3DAP) experiments [29–31, 33].

The interfacial segregation energy at the interface for precipitates with 100 at.% copper is larger than that for the precipitated phase with 50 at.% copper by 1.56 eV. This result indicates that interfacial segregation is strongly dependent on the composition of the precipitated phase and increases with its copper concentration. The strong dependence of interfacial segregation on the composition of precipitates plays an important role in experimental phenomena in which the concentration of aluminium at the interface of precipitates increases in ferritic steels during thermal treatment processes [29, 30, 33].

2. Nickel segregation

We find that the nickel segregation behaviour is similar to that of aluminium. The segregation energies (see ΔE_X^{Ni} in Table 2) of nickel in the interfaces are negative, indicating that the presence of nickel atoms in the interfaces is energetically favourable compared to that in the ferritic matrix. However, the most favourable sites depend on the composition of the precipitated phase. The most favourable sites are in the core region for the precipitated phase with 50 at.% copper, but at the interface for the precipitated phase with 100 and 75 at.% copper. These results indicate that nickel atoms can partition at the precipitates with 50 at.% copper and segregate into the interfaces of the precipitated phase with 100 and 75 at.% copper in a ferritic matrix. Therefore, nickel will segregate into the core region of the precipitates at the initial formation stage and be pushed away from the core towards the interface of the precipitates for the following growth stage. This is consistent with phase field [36] and Langer-Schwartz [37] simulations. These phenomena were also observed for the copper precipitates in RPV steels using 3DAP [27, 28].

The segregation energy of nickel at the interface also depends on the composition of the precipitated phase. The segregation energy at the interface of the precipitated phase with 100 at.% copper is larger than that of 50 at.% copper by 0.22 eV, a difference much lower than that of aluminium. This result indicates that the nickel concentration at the interface of copper-rich precipitates increases more slowly than that of aluminium with increasing copper concentration during the growth of precipitates. This trend has previously been observed in 3DAP experiments [55].

3. Chemical and mechanic contributions

As shown in Tables 1 and 2, the values of ΔE_X^{chem} approach those of ΔE_X , so long as the ΔE_X^{mech} is very small. These values indicate that chemical energy is the main contributor to the segregation behaviour of aluminium and nickel. ΔE_{sc} and ΔE_X are of comparable magnitude, implying that the relaxation energy per atom is much smaller than the interfacial segregation energy. The average relaxation energies per copper atom for precipitated phases with 100, 75 and 50 at.% copper are 0.012 eV, 0.027 eV, and 0.013 eV, whereas the smallest segregation energies of aluminium and nickel are 0.15 eV and 0.20 eV, respectively. These

values reflect the fact that the energy gains of the interfacial segregation of aluminium and nickel are much larger than that of lattice distortion.

It is necessary to discuss the factors affecting the relaxation energy of lattice distortion. The relaxation energy is mainly determined by mechanical stability and the mixing effects of the BCC FeCu metastable alloy. The mechanical stability and mixing effect both decrease with copper concentration (at copper concentrations > 50 at.%) [56, 57]. Higher mechanical stability reduces the relaxation energy, whereas larger mixing effects enhance the relaxation energy. Therefore, the relaxation energy of the precipitated phase with 75 at.% copper become the largest among the three structures studied due to the compromise formed between the effects of mechanical stability and mixing.

B. The Griffith work is influenced by segregation

We take the interface between the pure copper and ferritic matrix as a typical mode to analyse the Griffith work. The Griffith work is the energy separating an interface against the atomic cohesion. The influence of alloying element segregation on the Griffith work can be estimated by the value of $\Delta E_I^M - \Delta E_F^M$. We have calculated the segregation energies (ΔE_I^M) at the interface of precipitates in ferritic steels previously. Now, we calculate the segregation energies (ΔE_F^M) of aluminium and nickel at the fracture free surfaces, and the results are -0.78 and -0.51 eV, respectively. The value of $\Delta E_I^M - \Delta E_F^M$ for aluminium and nickel at the interface between pure copper and the ferritic matrix are -0.93 eV and 0.07 eV, respectively. As a result, the segregation of aluminium will enhance the interfacial cohesion, whereas the segregation of nickel will reduce the interfacial cohesion.

First, we discuss the electronic structures of aluminium and nickel segregation at the interface. The charge differences of aluminium and nickel at the interface are presented in the left-hand column of Fig. 3, showing that the charge accumulates in the interval region between atoms and is depleted in the inner atomic shells. The charge depletion region for aluminium atoms is larger than that of iron and copper atoms, because the 3s3p electrons of aluminium are more delocalised than the 3s3d electrons of iron and copper atoms. The 3p electrons of aluminium fill into the degeneration state of p_x , p_y , p_z , therefore the charge depletion region for the aluminium atom has a higher symmetry pattern. In contrast, the charge depletion region for the nickel atom is similar to that of iron and copper atoms,

because the valence states of nickel also include 3s3d. Because the delocalised electrons can be affected more by surrounding atoms, the segregation energy of aluminium is larger than that of nickel and more sensitive to the composition of the precipitated phase.

We now attempt to understand the effect of segregation on Griffith work by comparing the chemical bonding in the fracture free surface to that in the interface. The charge differences of aluminium and nickel at the fracture free surface are presented in the right-hand column of Fig. 3. Because the geometrical symmetry is broken for the free surface, the orbital p_z of aluminium state hybridises with the d_{z^2} of iron and becomes lower in energy. The only one p-electron of aluminium fills into p_z , and the p_{xy} is left unoccupied. This results stronger vertical bonding (Fe2-Al) and weaker lateral chemical bonding (Fe1-Al and Fe3-Al) of the free surface compared to that of the interface. The weakening effect of aluminium on lateral bonding contributes to a lower segregation energy at the free surface than that at the interface (by 0.93 eV). Therefore, $\Delta E_I^{Al} - \Delta E_F^{Al}$ for the segregation of aluminium is negative.

The alteration of the chemical bonding of nickel is totally different to that of aluminium. The spatial distribution of nickel at the fracture free surface is similar to that at the interface due to the d electron. The charge accumulations in the interval region of Fe1-Ni, Fe2-Ni, and Fe3-Ni for the free surface are all greater than that for the interface, indicating a stronger chemical bonding between these atoms at free surface. The enhanced chemical bonding arises from the contraction of bond lengths at the free surface. Because the chemical bonding at the free surface is stronger than at the interface, the segregation energy at the free surface is larger than at the interface (by 0.07 eV). $\Delta E_I^{Ni} - \Delta E_F^{Ni}$ for the segregation of nickel is consequently positive.

C. The embrittlement trend

The influence of alloying element M on an interfacial cohesive property is determined by both ΔE_I^M and $\Delta E_I^M - \Delta E_F^M$. We plot ΔE_I^M and $\Delta E_I^M - \Delta E_F^M$ for precipitated phases with different compositions in Fig. 4, showing that the values of ΔE_I^{Al} and $\Delta E_I^{Al} - \Delta E_F^{Al}$ strongly depend on the composition of the precipitated phase. The values of $\Delta E_I^{Al} - \Delta E_F^{Al}$ are positive for precipitated phases of 50 ~ 65 at.% copper and negative for precipitated phases of 65 ~ 100 at.% copper. Obviously, there is a wide range of compositions for the

precipitates whose interfacial cohesion are enhanced by aluminium segregation. The values of ΔE_I^{Al} for these precipitates are all larger than those of the precipitates whose interfacial cohesion is reduced by aluminium segregation. Therefore, aluminium segregation plays a prominent role in enhancing interfacial cohesion for copper-rich precipitates in ferritic steels.

In contrast, the values of ΔE_I^{Ni} and $\Delta E_I^{Ni} - \Delta E_F^{Ni}$ weakly depend on the composition of the precipitated phase. The value of ΔE_I^{Ni} varies weakly with the composition of the precipitated phase. The values of $\Delta E_I^{Ni} - \Delta E_F^{Ni}$ are all negative. These results indicate that nickel segregation can reduce the interfacial cohesion of copper-rich precipitated phases of any composition. Undoubtedly, nickel segregation plays a constant role in reducing interfacial cohesion for copper-rich precipitates in ferritic steels.

BCC copper-rich precipitates play important roles in dislocation pinning and misfit growth in ferritic steels. Dislocation pinning will strengthen the ferritic matrix, whereas the misfit growth will improve the ductility. The influence of the misfits produced by copper precipitates on ductile-brittle transformation has been proven to be considerable [58, 59]. The interfacial cohesive property and the amounts of precipitates present contribute importantly to ductile-brittle transformation. The ductile-brittle transition depend the competition between fracture stress and flow stress. Flow stress increases with decreasing temperature. When the flow stress is larger than the fracture stress at lower temperatures, the ferritic matrix is brittle; and when the flow stress is smaller than the fracture stress at higher temperatures, the ferritic matrix is ductile. Therefore, the DBTT can be altered by fracture stress, which is determined by the interfacial cohesion of precipitates. We can now predict that the segregation of aluminium can lower the DBTT due to the enhancing fracture stress of copper precipitates, whereas the segregation of nickel can increase the DBTT due to the reducing fracture stress of copper precipitates.

The nickel-induced interfacial embrittlement of copper-rich precipitates explains the observation that the DBTT of low-carbon, copper-precipitation-strengthened steels increase with nickel and copper content [58]. This effect also accounts for the observation that the shifts of DBTT in RPV steels after neutron irradiation are enhanced by the copper and nickel content [23, 24]. Furthermore, it can account for the observations that the influence of copper content on DBTT decrease is progressive when the nickel content decreases and the influence of nickel content on DBTT disappears for model alloys after neutron irradiation (at a neutron fluence of $72 \times 10^{18} m^{-2}$) with copper contents below 0.08 at.% (0.1 wt.%)

[25, 26].

IV. CONCLUSION

We have presented DFT-GGA calculations investigating the segregation behaviours of aluminium and nickel at the interface of precipitates in ferritic steels. We have examined the segregation energies of aluminium and nickel at the interface and within the core regions in precipitated phases with different compositions. Our results show that aluminium and nickel can segregate at the interface of precipitates in ferritic steels, in agreement with 3DAP experiments. Moreover, we also find that the interfacial segregation of aluminium is more sensitive to the composition of copper-rich precipitated phases than those of nickel. The most energetically favourable site of nickel segregation depends to the composition of the copper-rich precipitated phase. These detailed segregation behaviours are also consistent with 3DAP experiments.

We also calculated the contributions of aluminium and nickel segregation behaviours to Griffith work to predict the interfacial cohesive properties of precipitates and found that there are aluminium-induced ductility and nickel-induced embrittlement effects at the interface of precipitates. Aluminium-induced ductility arises mainly from the 3p electron of aluminium that causes weaker Fe-Al bonding at the fracture surface than at the interface. Nickel-induced embrittlement, however, is due mainly to the 3d electrons of nickel resulting in enhanced Fe-Ni bonding at the fracture surface compared to that at the interface. Finally, we have used the nickel-induced embrittlement at the interface of the copper precipitates in ferritic matrices to explain the experimental observation that the DBTT of low-carbon, copper-precipitation-strengthened steels and RPV steels increase with their nickel and copper content. These studies suggest a possibility of improving the ductility of ferritic steels from modifying interfacial cohesive properties of copper-rich precipitates by segregation of alloying elements.

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TABLE I: Segregation energies (in eV) of Al atoms at the interfaces and core regions of Cu-rich precipitated phases in a ferritic matrix, decompositions into chemical and mechanical contributions, and the relaxation energy of the supercell.

Site(X)	1	2	3	4
<i>α-Fe/prue BCC-Cu</i>				
$\Delta E_X^{chem,Al}$	0	-1.78	-1.52	-1.18
$\Delta E_X^{mech,Al}$	0	+0.07	+0.07	+0.06
ΔE_X^{Al}	0	-1.71	-1.45	-1.12
ΔE_{sc}	-0.60	-0.53	-0.53	-0.54
<i>α-Fe/BCC-CuFe(75 at.% Cu)</i>				
$\Delta E_X^{chem,Al}$	0	-1.07	-0.93	-0.60
$\Delta E_X^{mech,Al}$	0	-0.01	+0.02	-0.07
ΔE_X^{Al}	0	-1.08	-0.91	-0.67
ΔE_{sc}	-0.84	-0.85	-0.82	-0.91
<i>α-Fe/BCC-CuFe(50 at.% Cu)</i>				
$\Delta E_X^{chem,Al}$	0	-0.12	-0.13	0.14
$\Delta E_X^{mech,Al}$	0	-0.03	-0.03	-0.01
ΔE_X^{Al}	0	-0.15	-0.16	0.13
ΔE_{sc}	-0.28	-0.31	-0.31	-0.29

TABLE II: Segregation energies (in eV) of Ni atoms at the interfaces and core regions of Cu-rich precipitated phases in a ferritic matrix, decompositions into chemical and mechanical contributions, and the relaxation energy of the supercell.

Site(X)	1	2	3	4
<i>α-Fe/pure BCC-Cu</i>				
$\Delta E_X^{chem, Ni}$	0	-0.39	-0.42	-0.05
$\Delta E_X^{mech, Ni}$	0	-0.05	-0.01	-0.02
ΔE_X^{Ni}	0	-0.44	-0.43	-0.03
ΔE_{sc}	-0.43	-0.48	-0.44	-0.41
<i>α-Fe/BCC-CuFe(75 at.% Cu)</i>				
$\Delta E_X^{chem, Ni}$	0	-0.37	-0.33	-0.15
$\Delta E_X^{mech, Ni}$	0	-0.03	-0.04	-0.03
ΔE_X^{Ni}	0	-0.40	-0.38	-0.18
ΔE_{sc}	-0.73	-0.76	-0.78	-0.76
<i>α-Fe/BCC-CuFe(50 at.% Cu)</i>				
$\Delta E_X^{chem, Ni}$	0	-0.22	-0.24	-0.29
$\Delta E_X^{mech, Ni}$	0	-0.02	-0.03	+0.01
ΔE_X^{Ni}	0	-0.20	-0.27	-0.28
ΔE_{sc}	-0.24	-0.22	-0.27	-0.23

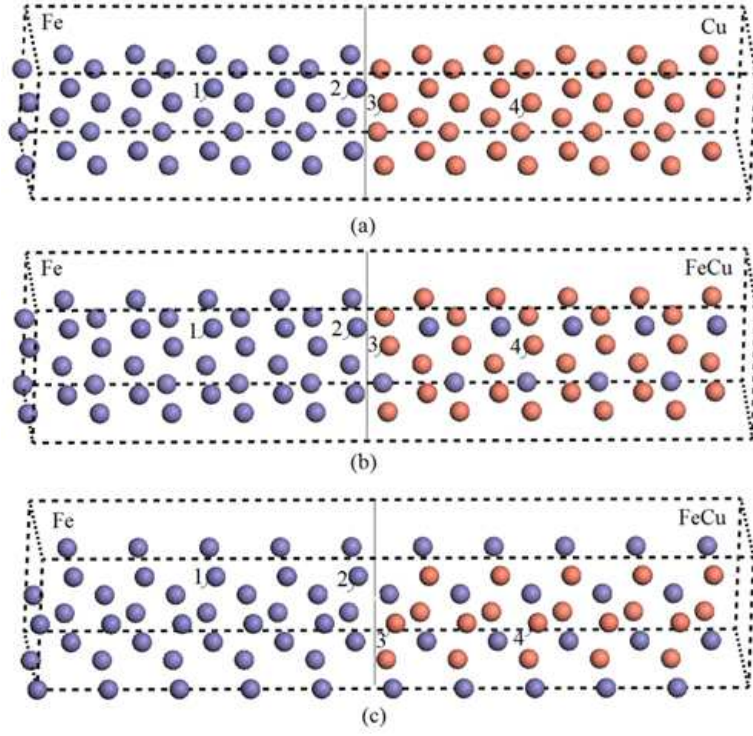


FIG. 1: The atomic structures of the (001) interfaces between BCC Cu-rich precipitated phases and ferritic matrix. The precipitated phases are Cu-Fe alloys with (a) 100 at.% (i.e., pure Cu), (b) 75 at.%, and (c) 50 at.% Cu concentration, respectively. Red and blue balls denote Cu and Fe atoms, respectively. The atoms marked by Arabic numerals denote the segregation sites in 1, the matrix; 2, the region of interface toward the matrix; 3, the region of interface toward the precipitated phase; and 4, the core region of the precipitated phase.

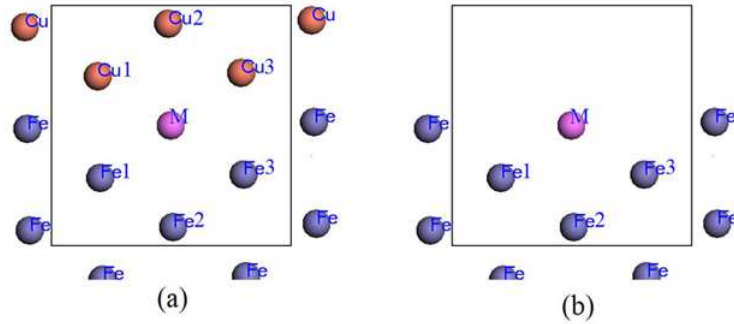


FIG. 2: Side view of the atomic structures of M segregation at (a) the interface between the BCC Cu-rich precipitated phase and the ferritic matrix and (b) its corresponding fracture free surface.

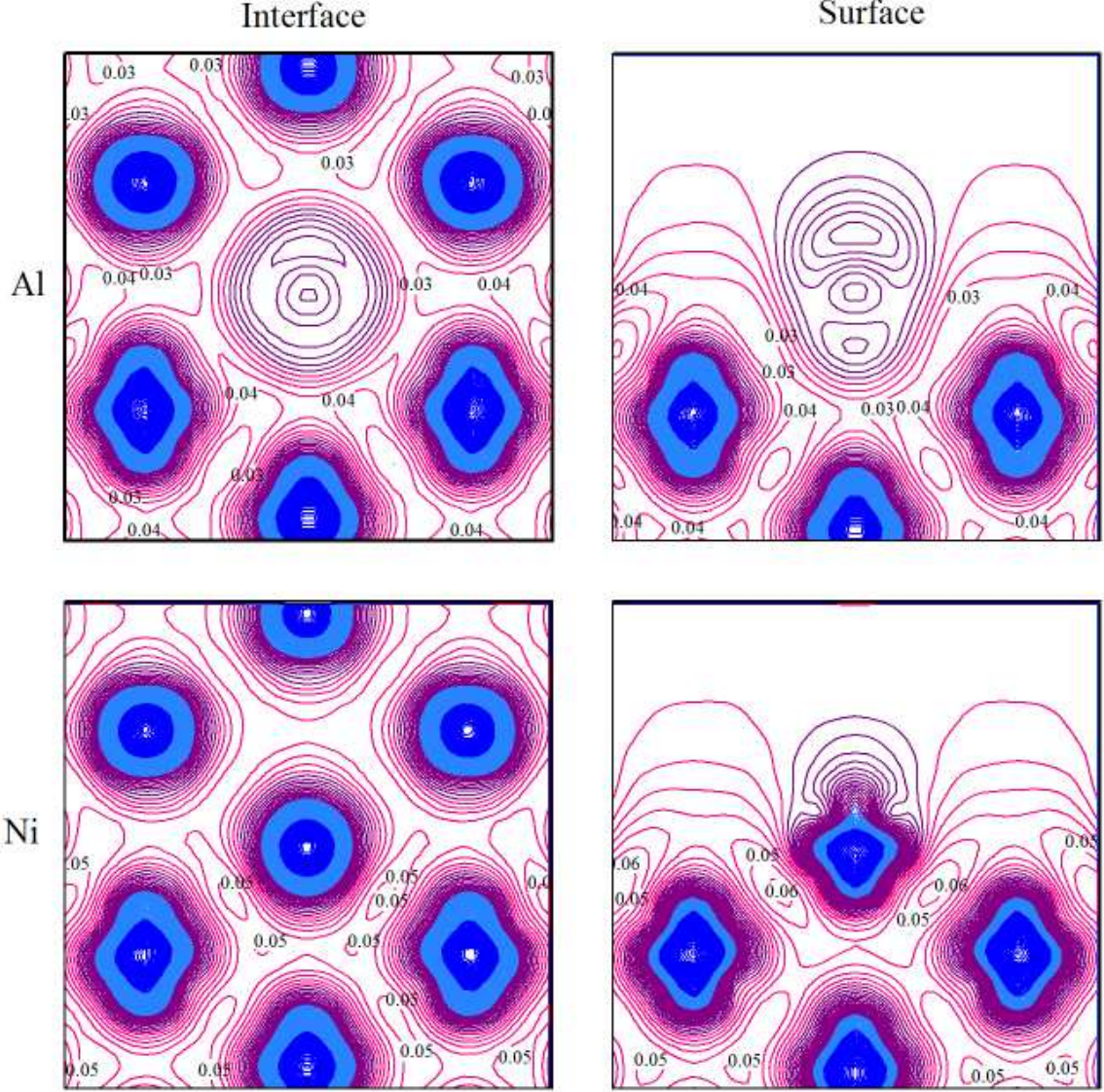


FIG. 3: The valence charge density differences of Ni at the interface (top left), Ni at the fracture free surface (top right), Al at the interface (bottom left), and Al at the fracture free surface (bottom right). Contours increase successively by a factor of $10^{-2}/\text{au}^3$. Blue, light blue, and purple lines denote charge depletion and pink lines denote charge accumulation. Regions displayed correspond to the square cell depicted in Fig. 2.

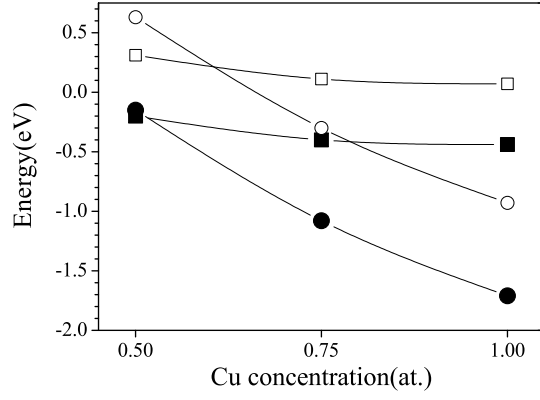


FIG. 4: ΔE_I^M (solid symbols) and $\Delta E_I^M - \Delta E_F^M$ (blank symbols) for Ni (squares) and Al (dots) segregating at the interfaces of the copper-rich precipitated phases with different copper concentrations in the ferritic matrix.